

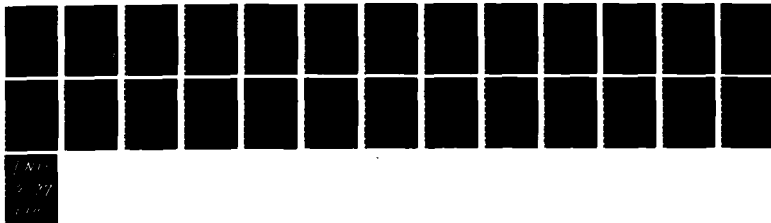
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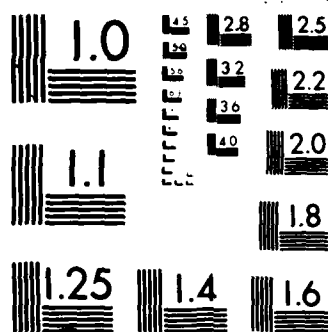
SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTALLINE
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Synthesis and Characterization of
Liquid Crystalline Poly(N-acylethyleneimine)s

By

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ABSTRACT

The synthesis of three cyclic imino ethers containing mesogenic groups attached to the heterocyclic unit through flexible spacers is described. Cationic ring opening isomerization polymerization of two of them, i.e., 2-[4-(4-methoxy-4'-biphenyloxy)butyl]-2-oxazoline (MeOBiph-4-Oxz) and 2-[6-(4-methoxy-4'-biphenyloxy)hexyl]-2-oxazoline (MeOBiPh-6-Oxz) provided thermotropic liquid crystalline (LC) poly(N-acylethylene-imine)s, while the polymerization of 2-[4-(4-phenylphenoxy) butyl]-2-oxazoline (BiPh-4-Oxz) led to a crystalline polymer.

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Side-chain thermotropic liquid crystalline polymers

Synthesis and Characterization of
Liquid Crystalline Poly(N-acylethyleneimine)s

by

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Summary

The synthesis of three cyclic imino ethers containing mesogenic groups attached to the heterocyclic unit through flexible spacers is described. Cationic ring opening isomerization polymerization of two of them, i.e., 2-[4-(4-methoxy-4'-biphenyloxy)butyl]-2-oxazoline (MeOBiPh-4-Oxz) and 2-[6-(4-methoxy-4'-biphenyloxy)hexyl]-2-oxazoline (MeOBiPh-6-Oxz) provided thermotropic liquid crystalline (LC) poly(N-acylethylene-imine)s, while the polymerization of 2-[4-(4-phenylphenoxy) butyl]-2-oxazoline (BiPh-4-Oxz) led to a crystalline polymer.

Introduction

Thermotropic side-chain liquid crystalline (LC) polymers have received considerable research interest only after Finkelmann and Ringsdorf (1,2) had introduced the flexible spacer concept. This field has been recently reviewed (3,4,5). Research in our laboratory has been mainly focussed on the role of interconnecting structural units between the mesogen and the spacer in main-chain LC polymers (6-9) or between the side-chain mesogen and the polymer backbone (10) in side-chain LC polymers, in order to establish structural requirements required for the design of functional LC polymers.

Cyclic imino ethers, particularly 2-substituted-2-oxazolines are a class of extensively studied monomers which can be polymerized by cationic initiators to produce linear poly(N-acylethylenimine)s. 2-Oxazolines undergo also a large variety of ring-opening addition reactions. Several recent publications review both types of reactions described above (11-13).

The goal of this paper is to present the synthesis of the first examples of thermotropic LC poly(N-acylethylenimine)s.

Experimental

A. Materials

All the reagents (Aldrich and Lancaster Synthesis) were used as received, except the polymerization solvents which were purified and dried by conventional techniques used to achieve the purity required for cationic polymerization. 4-Methoxy-4'-hydroxybiphenyl was synthesized as previously described (10). Ethylene glycol ditosylate was synthesized according to a literature method (14).

B. Techniques

^1H -NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer in CDCl_3 solutions and with TMS as internal standard. A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions which were read at the maximum of their endothermic or exothermic peaks. In all cases heating and cooling rates were $20^\circ\text{C}/\text{min}$. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. After the first heating scan, the sample was "annealed" at about 10°C above the isotropization temperature for 5-10 min. Under these registration conditions, beginning with the second heating and cooling scans all the DSC scans produced perfectly reproducible data. The transitions reported were read during the second or third heating and cooling scans. A Carl Zeiss optical polarizing microscope (magnification: 100x) equipped with a Mettler FP82 hot stage and a Mettler FP80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures (8-10).

C. Synthesis of the Monomers

Two synthetic procedures were used for the preparation of the monomers. Both methods are outlined in Schemes 1 and 2. An example for each of them is described below.

Ethyl-5-(4-phenylphenoxy)Valerate (BiPh-4-COOEt)

4-Phenylphenol (8g, 0.04 mol) and 1.656g (0.04 mol) of NaOH were dissolved in 100 ml of methanol. Methanol was evaporated in a rotary evaporator and the sodium phenolate obtained was dried under vacuum. The sodium salt of 4-phenylphenol was put into 120 ml of dried dimethylformamide and 8.5 ml (0.054 mol) of ethyl-5-bromovalerate and 1.4g (10 mol% versus phenol) of tetrabutylammonium hydrogen sulfate were added. The reaction mixture was stirred at 80°C overnight and then poured into water. The precipitated product was filtered, dried and recrystallized from methanol to yield 9g (75%) of white crystals. m.p., 72-74°C.

2-Hydroxyethyl-5-(4-phenylphenoxy) Valeramide (BiPh-4-Hydroxyamide)

Ethyl-5-(4-phenylphenoxy) valerate (7g, 0.024 mol) was dissolved in 50 ml (large excess) of ethanolamine and catalytic traces of p-toluensulfonic acid were added. The solution was stirred at 150°C for 20 hrs and then the excess of ethanolamine was distilled off under vacuum. The product left after distillation was purified by recrystallization from methanol to yield 7g (95%) of white crystals. m.p., 146-148°C.

2-[4-(4-Phenylphenoxy) butyl]-2-oxazoline (BiPh-4-OXZ)

2-Hydroxyethyl-5-(4-phenylphenoxy) valeramide (6.9g, 0.022 mol) was dissolved in 60 ml of dried methylene chloride and cooled to 0°C in an ice-water bath. Thionyl chloride (2.5 ml, 0.035 mol) was added dropwise, and the solution was left to warm up to room temperature. The solvent was evaporated in a rotary evaporator

at room temperature, and the chloroamide obtained was dissolved in 100 ml of absolute ethanol. To this solution, 0.92g (0.04 mol) of sodium metal dissolved in 50 ml of absolute ethanol were added, and the mixture was heated to reflux for 1 hr. Then the ethanol was evaporated, and the solid product obtained was washed with water, dried and purified by recrystallization from hexane to yield 4.2g (65%) of white crystals. m.p., 87-89°C.

4'-(6-Cyanohexyloxy)-4-Methoxybiphenyl (MeOBiPh-6-CN)

4-Methoxy-4'-hydroxybiphenyl (5g, 0.025 mol) and 1.68g (0.03 mol) of KOH were dissolved in 100 ml of ethanol. 7-Bromoheptanenitrile (4.5 ml, 0.03 mol) was added and the reaction mixture was heated to reflux. After 15 hr, the reaction mixture was poured into water and the precipitate was filtered off, dried and recrystallized from ethanol to yield 6.4g (83%) of white crystals. m.p., 116-118°C.

2-[6-(4-Methoxy-4'-biphenyloxy)hexyl]-2-Oxazoline (MeOBiPh-6-Oxz)

MeOBiPh-6-CN (6g, 0.019 mol) and 0.112g (4.9×10^{-4} mol) of cadmium acetate dihydrate were heated in a round bottom flask equipped with septums, and magnetic stirrer, under argon atmosphere to 130°C. 3 ml (0.021 mol) of freshly distilled ethanolamine were added dropwise with a syringe and the reaction mixture was left stirring at this temperature for 24 hrs. Then it was cooled to room temperature

and dissolved in chloroform. The chloroform solution was washed with water, dried, passed through a short chromatographic column containing basic alumina, and the solvent was evaporated in a rotary evaporator. The white crystalline product obtained was purified by recrystallization from a mixture of cyclohexane and benzene (9/1 vol/vol) to yield 4.7g (70%) of white crystals. m.p., 104-107°C.

2-[4-(4-Methoxy-4'-Biphenyloxy)butyl]-2-Oxazoline (MeOBiPh-4Oxz)

MeOBiPh-4-Oxz was synthesized by a similar procedure to that used for the synthesis of MeOBiPh-6-Oxz. The chemical shifts obtained from the 200 MHz ^1H -NMR spectra of all the monomers and intermediary compounds are listed in Table 1, together with their melting points.

Polymerizations

Cationic polymerizations of the monomers were performed in Schlenk tubes equipped with septums, under argon after the solid monomers were degassed. In the case of solution polymerizations, solvents were distilled directly into the polymerization tubes, while the initiators were inserted with syringes as solutions. Polymerizations were terminated with methanol containing traces of NH_3 . All polymers were purified by precipitation from hot DMF solutions into methanol. Table 2 summarizes the polymerization results.

Scheme 1 outlines the synthetic method used for the preparation of BiPh-4-Oxz. It follows a conventional route which has been frequently employed for the synthesis of 2-substituted 2-oxazolines (14,15). As it has been presented in the experimental section, each reaction step was achieved with high conversion without any difficulties. MeOBiPh-4-Oxz and MeOBiPh-6-Oxz were synthesized according to Scheme 2. This method was adopted for these two monomers mainly because the hydroxyamide derivatives of 4-methoxy-4'-oxybiphenylene present a quite low solubility in comparison to those of the corresponding 4-phenylphenoxy derivatives. The lower solubility required large amounts of solvents and decreased the yields in the subsequent steps. Therefore, for the synthesis of these two monomers we adopted a method based on a procedure initially developed by Witte and Seeliger (16-17). This method proved to work well also for the synthesis of other 2-substituted-2-oxazolines (18). The only difficulty encountered by this procedure consists in a tedious separation of the unreacted MeOBiPh-6-CN and MeOBiPh-4-CN from the resultant 2-oxazolines by column chromatography.

Table 2 summarizes the cationic ring-opening isomerization polymerization of the cyclic imino ethers containing mesogenic side groups. Both bulk and solution polymerizations were employed with ethyleneglycol ditosylate or trifluoromethanesulfonic anhydride as initiators. The rate constant of propagation is higher than the rate constant of initiation when tosyl esters are used as initiators for the polymerization of 2-substituted-2-oxazolines (11). Therefore, ethyleneglycol ditosylate was used as initiator in an attempt to obtain polymers with higher molecular weights than those expected to form with a monotosylated initiator. Conversions were 100% for bulk polymerizations and higher than 50% for solution polymerizations. The obtained polymers

present very low solubilities being soluble in DMF only at 120°C and in anisole at 150°C. At the same time all polymers undergo thermal transitions at high temperatures (Table 2). Therefore, the control of the polymers molecular weights through the initial ratio between the monomer and initiator was difficult to achieve. Determination of the polymer molecular weights was not possible. Under the polymerization conditions presented in Table 2 all polymers precipitated out of the reaction mixture. For the polymerizations performed in solution (no. 2 and 3 from Table 2), the polymerization temperature was increased after the polymers precipitated out of the reaction mixture. Under these circumstances, T_g from Table 2 did not increase up to the values of the polymers obtained in bulk, and this means that the highest molecular weight polymers were obtained by bulk polymerization.

Figure 1 shows some representative DSC heating and cooling traces for the poly(BiPh-4-Oxz), (sample no. 6 from Table 2). Curve A represents the heating scan (20°C/min) after this sample was quenched from 230°C to 20°C. It shows a glass transition temperature (T_g) at 57°C, followed by a crystallization exotherm at 82°C and a melting transition at 178°C. The following cooling scan (20°C/min) is presented as curve B. It shows a crystallization exotherm at 109°C. Curve C is the heating scan (20°C/min) after this sample was cooled at 20°C/min. This time the T_g is at a higher temperature than in curve A, i.e., 84°C, while the melting endotherm appears again at 178°C. Our conclusion is that this polymer is not liquid crystalline but crystalline only. The following arguments are supporting a crystalline structure for this polymer. Crystallization temperature is 69°C supercooled versus the melting endotherm. Usually, liquid crystalline

transitions, although appear to be supercooled particularly when the polymer molecular weight is low, are less supercooled than the crystalline transitions (19,20). At the same time on quenching a liquid crystalline polymer from the isotropic phase, is very difficult to obtain a frozen-in isotropic phase below T_g as curve A would suggest. Therefore, we can safely conclude that poly(BiPh-4-Oxz) is crystalline.

This is not an unexpected result. The insertion of 4-phenylphenol as side group in polymers before, did give rise to a liquid crystalline polymer in one case only, i.e., poly(biphenylacrylate) (21). Extensive research performed by Magagnini et. al., (21-28) on this mesogen could not provide another example of liquid crystalline polymers containing 4-phenylphenol and, therefore, poly(4-biphenylacrylate) is still the only exception from the spacer concept introduced by Finkelmann and Ringsdorf (1,2). It is not unexpected that poly(BiPh-4-Oxz) gives a crystalline polymer if we have in mind the ease of crystallization of many poly(N-acyl ethyleneimine)s containing bulky pendant groups (29), and the fact that atactic poly 1-[6-(4-biphenyloxy) hexyloxycarbonyl]ethylene is a crystalline polymer (28).

Figure 2 shows typical heating (A) and cooling (B) DSC scans exhibited by poly(MeOBiPh-4-Oxz) (sample no. 1 from Table 2). The heating scan presents the same behavior independent of the thermal history of the sample. Even when this sample was quenched in liquid N_2 , it did not present a crystallization exotherm on the next heating scan. At the same time the endotherm from $228^{\circ}C$ is only supercooled $41^{\circ}C$ on the cooling scan. Therefore, we can consider that these two

transitions are due to isotropization (T_i). As we can see from Table 2 (no. 1-4) T_i is molecular weight dependent. Solution polymerizations give polymers with lower T_i values than the polymers obtained in bulk. Therefore, bulk polymerizations led to higher molecular weight polymers. Analysis of this sample by optical polarization microscopy demonstrated an anisotropic smectic type mesomorphism which is characterized by high viscosity below T_i . The glass transition temperature for these polymers could not be exactly assigned, and this is not unusual for smectic side-chain liquid crystalline polymers (10).

Figure 3 presents several heating scans and one cooling scan for poly(MeOBiPh-6-Oxz). The heating scans were all obtained at $20^{\circ}\text{C}/\text{min}$, but they underwent different previous thermal treatments. Scan A was obtained after the polymer was quenched from 220°C into liquid nitrogen. No cold crystallization could be observed. Scan B was obtained after quenching from 220°C at $320^{\circ}\text{C}/\text{min}$ to room temperature, while scan C represents the heating scan obtained after cooling the sample at $20^{\circ}\text{C}/\text{min}$. All heating scans present multiple transitions which are only slightly affected by the thermal history of the sample. Comparing the three heating scans we see that the first endotherm at 160°C can hardly be discussed because of its overlap with the next transition. The second endotherm at 182°C (scan A) does shift towards higher temperatures when the rate of the previous cooling scan is decreasing. Apparently, it moves to 186°C (scan B) and 196°C (scan C). The last endotherm at 200°C (scan A), 200°C (scan B) and 202°C (scan C) is the least affected and therefore, can be assigned to isotropization. In scan C a new endotherm appears at 173°C and it certainly could be attributed to a melting transition. Therefore, transition temperatures below this melting should be due

to different size crystallites. Tentatively, we can consider that the transitions at 182, 186 and 196°C (scans A,B and C) are due to a liquid - crystalline - liquid - crystalline transitions. Optical microscopy indicates smectic mesomorphism in between the last two transitions. On cooling scans, there are two exotherms; the first one at 161°C can be assigned to isotropization while the one at 153°C to crystallization.

It is interesting at this point to compare the behavior of poly(MeOBiPh-6-Oxz) with that of the corresponding polymethacrylate containing also six methylene units as a spacer (2,30), (Scheme 3).

This polymethacrylate was reported by Ringsdorf et. al, and its phase behavior is known both for the atactic (2,30) and isotactic (30) configurations. The atactic polymer is crystalline and melts at 117-119°C into a smectic mesophase. The isotropization temperature is 127-131°C. The isotactic polymer is crystalline and melts at 131°C into a smectic mesophase. Its isotropization temperature is 135°C. No glass transition temperature could be detected for any of the two polymers, and as we have mentioned previously this is quite characteristic for smectic or highly crystalline polymers. The isotactic polymer presents both higher melting and isotropization temperatures than the atactic polymer and this overall result is due to the highly organized isotactic backbone. The substituted poly(N-acylethyleneimine)s present even higher meltings and isotropizations than the isotactic polymethacrylate. This can be explained first as being a consequence of its highly ordered backbone. The second reason for it is that the interconnecting group between the backbone and spacer is an amide group which is less flexible than the ester groups present in polymethacrylates. In a previous paper from our laboratory (10) we have demonstrated that poly(vinyl

ether)s and poly(propenyl ether)s containing similar spacers and mesogens present lower thermal transitions than the corresponding polymethacrylates. Based on these results we have concluded that the interconnecting group between spacer and backbone plays an important role in the decoupling of the mesogenic units. The presence of amide groups in between spacer and mesogen do not favor the decoupling of the mesogen and this is in agreement with our previous results on both main chain (6-9) and side-chain (10) liquid crystalline polymers. These results are also in agreement with the phase behavior of main chain thermotropic polyamides (31) and of side chain poly(methacrylamide)s (3,4).

Acknowledgements

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Figure Captions

Figure 1. Normalized DSC thermograms for poly(BiPh-4-Oxz) (sample no. 6 from Table 2): A) heating scan ($20^{\circ}\text{C}/\text{min}$) after quenching from 230°C to 20°C ; B) cooling scan ($20^{\circ}\text{C}/\text{min}$) after scan A; C) heating scan ($20^{\circ}\text{C}/\text{min}$) after scan B.

Figure 2. Normalized DSC thermograms for poly(MeOBiPh-4-Oxz) (sample no. 1 from Table 2): A) heating scan ($20^{\circ}\text{C}/\text{min}$), independent of the previous cooling scan rate; B) cooling scan ($20^{\circ}\text{C}/\text{min}$).

Figure 3: Normalized DSC thermograms for poly(MeOBiPh-6-Oxz) (sample no. 5 from Table 2): A) heating scan ($20^{\circ}\text{C}/\text{min}$) after quenching from 220°C into liquid nitrogen; B) heating scan ($20^{\circ}\text{C}/\text{min}$) after quenching from 220°C to 20°C at $320^{\circ}\text{C}/\text{min}$; C) heating scan ($20^{\circ}\text{C}/\text{min}$) after cooling from 220°C to 20°C at $20^{\circ}\text{C}/\text{min}$; D) cooling scan ($20^{\circ}\text{C}/\text{min}$).

List of Schemes

Scheme 1. Synthesis of BiPh-4-Oxz.

Scheme 2. Synthetic route used for the preparation of MeOBiPh-n-Oxz, $n = 4,6$.

Scheme 3. Structural units of poly(N-acyl ethyleneimine) and polymethacrylate containing the 6-(4-methoxy-4'-biphenyloxy) hexyl side group.

TABLE I

Characterization of 2-Substituted-2-Oxazolines

Compound	mp(°C)	¹ H-NMR, δ (ppm)
MeOBiPh-4-CN	137-139	1.90(m, -CH ₂ CH ₂ -); 2.40(t, -CH ₂ CN); 3.80(s, CH ₃ O-); 4.00(t, -CH ₂ OPh); 6.90 and 7.40(m, 8 aromatic protons).
MeOBiPh-4-Oxz	114-117	1.83(m, -CH ₂ CH ₂ -); 2.33(t, -CH ₂ C); 3.80(m, CH ₃ O- and -CH ₂ N=); 4.00(t, -CH ₂ OPh); 4.20(t, -CH ₂ O-); 6.91 and 7.43(m, 8 aromatic protons).
MeOBiPh-6-CN	115-117	1.34-1.95(m, -CH ₂ CH ₂ CH ₂ CH ₂ -); 2.34(t, -CH ₂ CN); 3.83(s, CH ₃ O-); 3.96(t, -CH ₂ OPh) 6.90 and 7.40(m, 8 aromatic protons).
MeOBiPh-6-Oxz	104-107	1.34-1.95(m, -CH ₂ CH ₂ CH ₂ CH ₂ -); 2.29(t, -CH ₂ C); 3.83(m, CH ₃ O- and -CH ₂ N=); 3.96(t -CH ₂ OPh); 4.20(t, -CH ₂ O-); 6.91 and 7.46(m, 8 aromatic protons).
BiPh-4-COOET	72-74	1.23(t, CH ₃ -); 1.83(m, -CH ₂ CH ₂ -); 2.38(t, -CH ₂ C=O); 4.10(m, -CH ₂ OPh and -CH ₂ O-) 6.85 to 7.80 (9 aromatic protons).
BiPh-4-Hydroxyamide	146-148	1.65(m, -CH ₂ CH ₂ -); 2.15(t, -CH ₂ C=O); 3.15 and 3.40(m, -NCH ₂ CH ₂ OH); 3.97(t, -CH ₂ OPh); 6.91 to 7.83 (9 aromatic protons).
BiPh-4-Oxz	87-89	1.85(m, -CH ₂ CH ₂ -); 2.34(t, -CH ₂ C); 3.80(t, -CH ₂ N=), 4.00(t, -CH ₂ OPh), 4.17(t, -CH ₂ O-); 6.88 to 7.60(m, 9 aromatic protons).

TABLE 2

Cationic Polymerization of Substituted 2-Oxazolines and Thermal Characterization of the Resulting Polymers

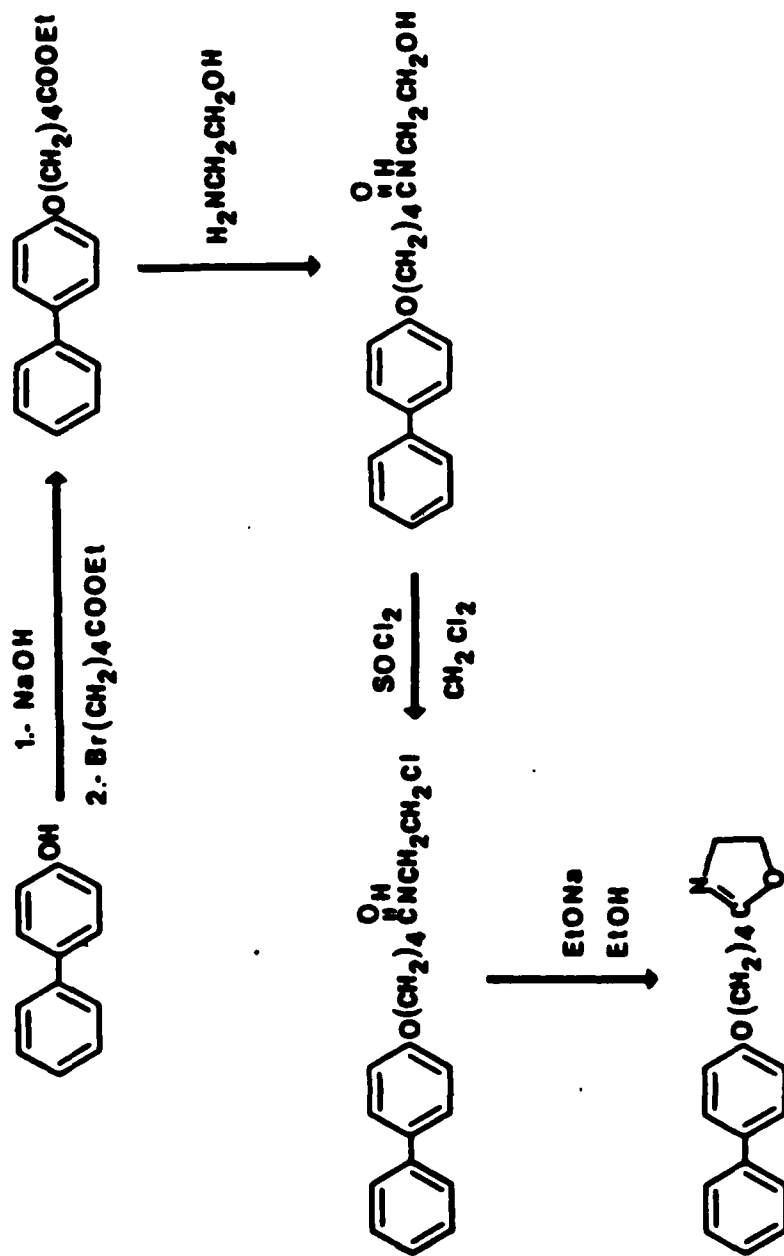
No.	Monomer	Solvent ^{a)}	Polym. Temp. (°C)	Polym. Time (hr)	Initiator	[M]/[I] (mole/mole)	Conversion (%)	Thermal Transition(°C)									
								Heating				Cooling ^{b)}					
								T _g	T ₁	T ₂	T ₃	T ₄	T _g	T ₁	T ₂	T ₃	T ₄
1	MeOBiPh-4-Oxz	BULK	140	15	EGT ^{b)}	438	100	---	---	---	---	228	---	---	---	---	187
2	"	DMP	100 [*] 120	15 6	"	100	50	---	---	---	163	175	N.A.				
3	"	ANISOLE	130 [*] 150	15 2	"	100	72	---	---	---	---	219	---	---	---	---	180
4	"	BULK	140	15	TPMSA ^{c)}	100	100	---	---	---	---	223	N.A.				
5	MeOBiPh-6-Oxz	BULK	140	15	EGT ^{b)}	100	100	---	155	173	196	202	---	---	---	153	161
6	BiPh-4-Oxz	BULK	140	15	EGT ^{b)}	100	100	84	---	---	---	178	---	---	---	---	109

a) Monomer concentration: 10% (W/Vol)

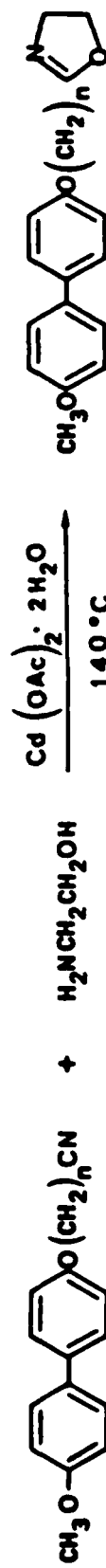
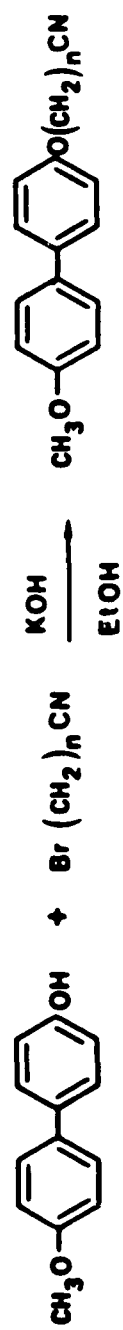
b) EGT: Ethyleneglycol ditosylate

c) TPMSA: Trifluoromethanesulfonic anhydride

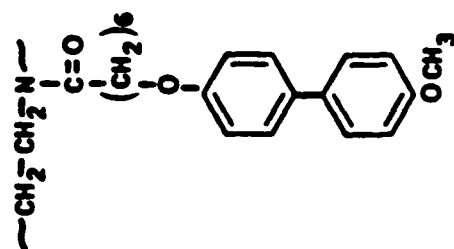
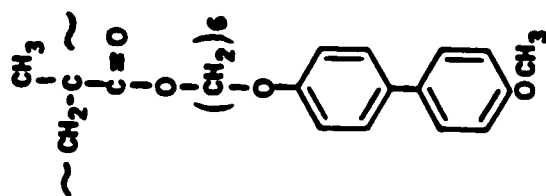
* Polymer precipitated at this temperature



Scheme 1



Scheme 2



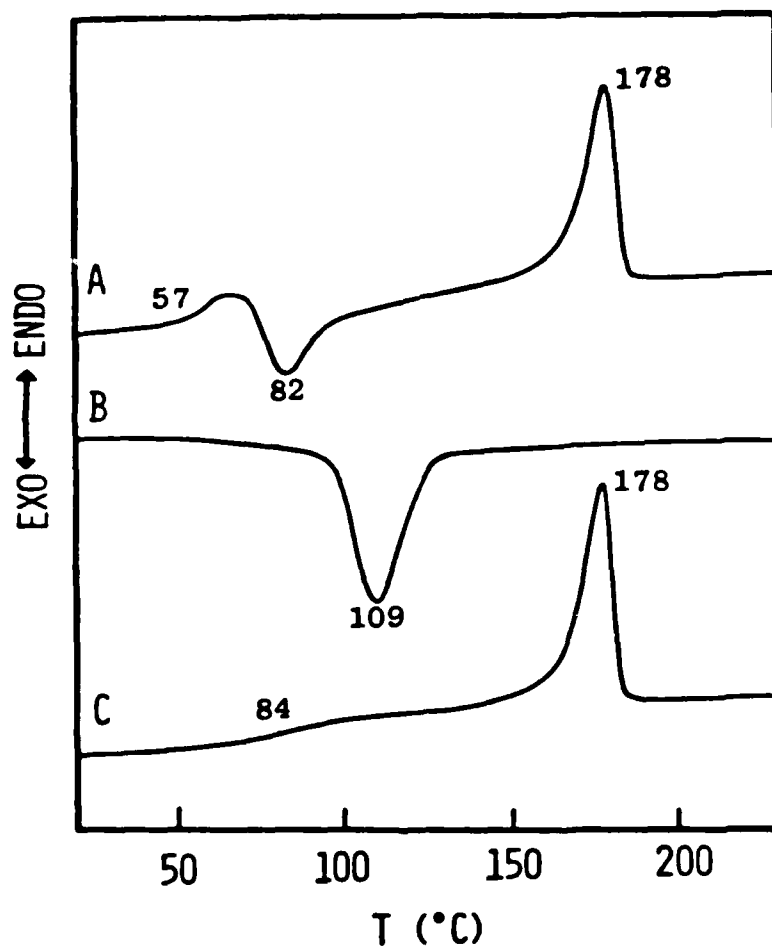


Fig. 1

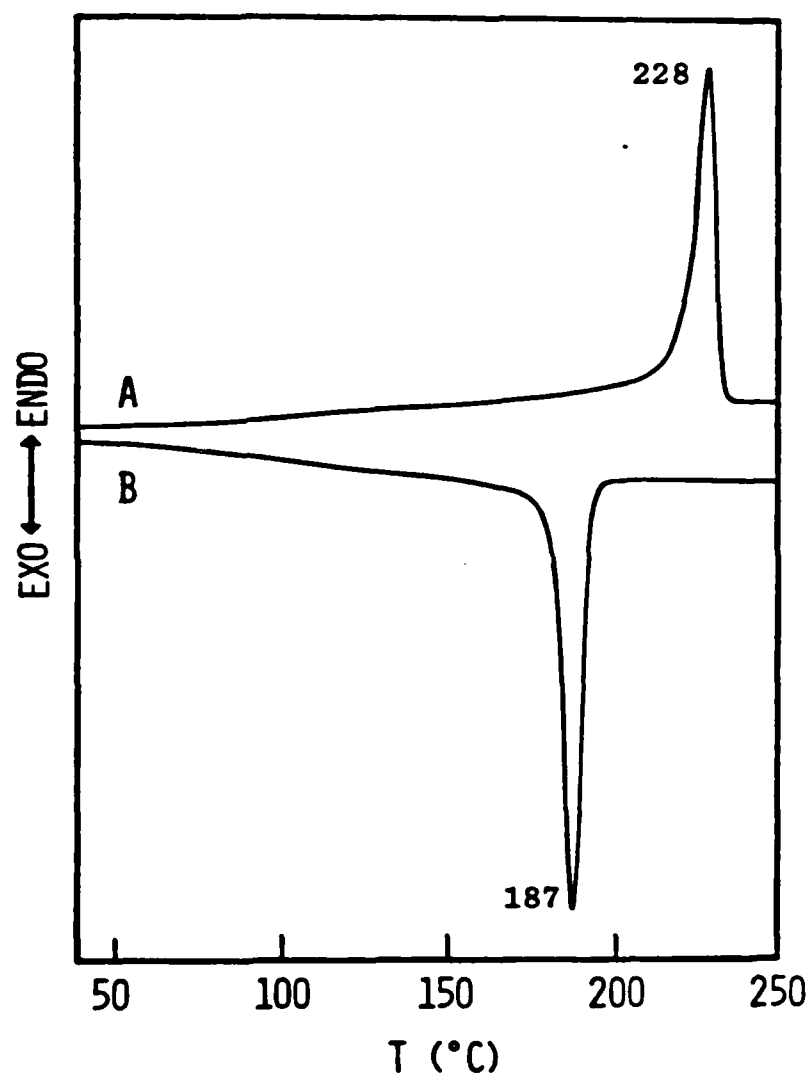
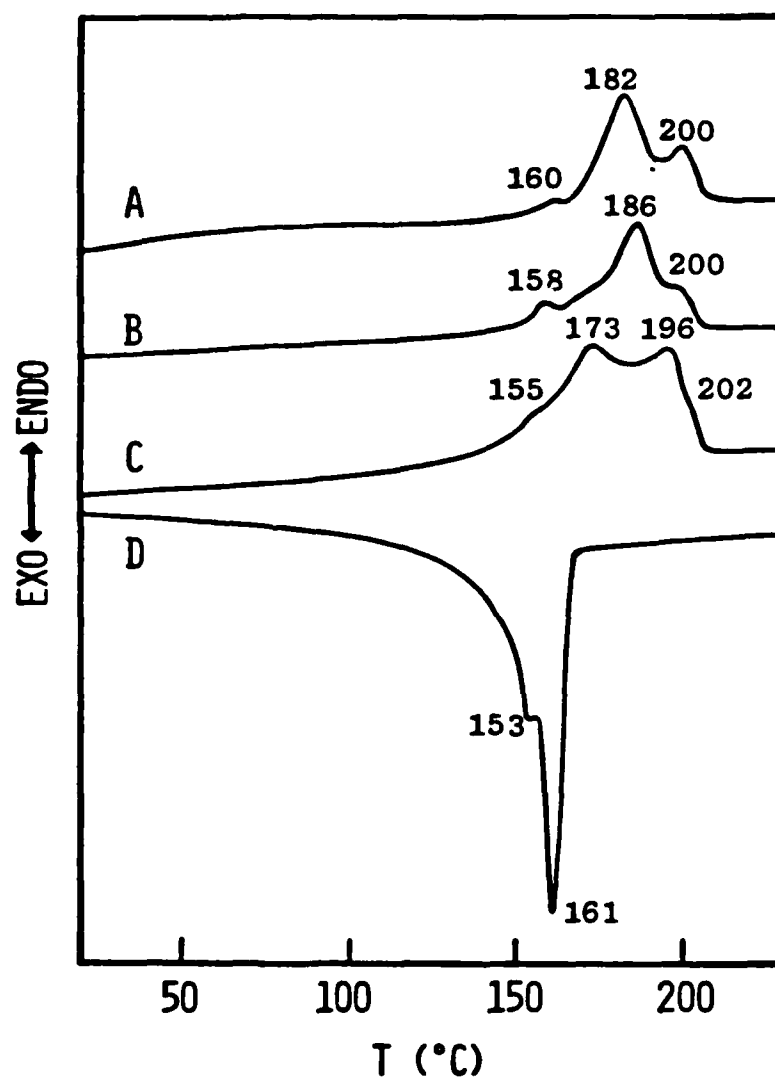


Fig. 2



END

2-87

DTIC